

analysis

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JADED CRUSADERS

The early seventies was the high point in public arousal concerning environmental issues. Almost every perceived threat to the environment was the signal for the creation of a protest group. An environmental ethic was enunciated opposing any action which was judged to degrade the environment. While combatting pollution of air, land and water was the focal point of concern, under this broad banner flocked opponents of expressways, high-rise developments, airports and urban sprawl. An apparent massive groundswell of popular support was generated on behalf of these varied causes. The groups were influential in effecting changes in policies or programs, and consequently were judged to have achieved their objectives.

The apparent victories had some hidden costs which can only be measured in human terms. Many of these battles were fought with a religious fervour, with issues presented in black and white terms. The worst of these righteous saviours were, in the words of Yeats, "full of passionate intensity". Those who challenged or opposed the crusaders were labelled infidels who had sold out to powerful, money-grabbing, ungodly interests. Attacking the integrity of public servants by veiled innuendoes, wild charges and false accusations was commonplace, and particularly effective since they were unable to publicly defend themselves.

Where have all the strident voices gone? Most of these groups have now disbanded. Some were one-issue affairs, others coalitions brought together to present a united front on matters now resolved, while some were of the trendy category whose early demise was predictable. Some of the larger groups have shown more staying power, and become hybrid, quasi-university-government-private sector institutions. These survivors now have muted voices, and tend to be less categorical in their statements on environmental issues. Whether this more responsible stance is attributable to their reliance on government sources for part of their funding, or a latter-day realization that all environmental issues cannot be reduced to simplistic terms, is anyone's guess.



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Much good was accomplished by those activists who genuinely sought to rally public support for the environmental cause, and in the process refrained from indulging in crisis-mongering and character assassination. Their contribution, however, was marred by the actions of those on the lunatic fringe of the environmental movement.

The public spotlight has now switched to jobs, inflation, energy. But the environmental work "in the trenches" still goes on. The unglamorous inspections, monitoring, testing, enforcement, and negotiation is daily carried out. Small gains in strengthening legislation, toughening standards, reducing emissions, are the real criteria of advances in environmental protection.

The polemics and purple rhetoric of the "townhouse environmentalist era" has finally faded away. No longer are we daily berated by the pedantic, leather-tongued oracles of a pristine environment. Good riddance.

MUTAGENIC ASSAYS METHOD DEVELOPMENT

Very little is known concerning the human health effects of a large number of the chemicals present in the environment. This knowledge gap is particularly worrisome with respect to compounds which may manifest detrimental health effects decades after the original exposure. Since in the past apparently innocuous compounds have been shown to possess mutagenic or carcinogenic properties, this concern is fully warranted.

The most definitive means for assessing the potential hazard of a substance involves its application to laboratory animals. The capital costs, and the time required for effects to develop and be observed make this approach prohibitive. On the other hand much less costly microbiological methods for measuring mutagenic properties of organic compounds have been developed which have been successful in identifying 90% of tested carcinogenic substances. The Laboratory Services Branch's Biohazard Unit has been recently organized to adapt such methods for use on drinking waters, water treatment effluents and other environmental water samples.

The approach being taken includes the use of the "Ames" test for confirming mutagenic compounds in order to establish experience with the procedure. Priority compounds under study include chlorinated organics, petrochemical products and their wastes, and polyaromatic hydrocarbons. This bacteriological assay will be supplemented by mycological (yeast) assay procedures.

Since it can be anticipated that only a small percentage of environmental samples will yield positive results, and those that do will show only very low levels of mutagenic activity, it will be necessary to develop a screening procedure for presence/absence of activity. Techniques for concentration of mutagenic substances from those samples displaying activity will be required and several procedures are being developed.

When a sample is found to be mutagenically active, it will be subjected to chemical fractionation for further testing. When the mutagenic component is isolated and identified it will be tested by expanded assays to quantify its activity.

(Dr. D. Rokosh - (416) 248-3001)

ANALYSIS OF PRECIPITATION SAMPLES

The use of fossil fuels, manufacturing processes and various smelting operations produce oxides of nitrogen and sulfur. These are oxidized in the atmosphere and react with water to form acids, the entrainment and precipitation of which, in rain or snow, has become a major concern in Ontario. Many of the lakes in Northern Ontario have a very low alkalinity and are therefore unable to resist indefinitely the effect of acid precipitation which reacts to lower the pH.

Lowering the pH level in lakes and streams adversely affects the fish population and also has a deleterious impact on the lake productivity. If corrective action is to be taken, accurate estimates are required of the rate of acid fallout and the capacity of the lakes to resist acidification. The requisite improved techniques for low level alkalinity, acidity and cation/anion balance have been developed and are presently being tested in the Laboratory Services Branch.

A microprocessor-controlled titration permits analysis for acidity/alkalinity to within 0.1 mg/liter at the 2 mg/liter CaCO_3 level. During the titration a Gran plot interpolation is used to calculate the exact inflection point of the titration curve in order to achieve the greater accuracy and precision required. Previous methods resulted in an over-estimation of the true alkalinity of samples and the bias was most pronounced at low levels.

To facilitate ion balance calculations, the novel analytical technique of ion chromatography is being used to scan for fluoride, chloride, nitrite, phosphate, bromide, sulfite, nitrate and sulfate in precipitation samples. These anions are separated by ion exchange on a separator column, converted to their acid forms on a strong acid cation exchange resin, and the concentrations are determined using a conductivity detector. This system is much more sensitive for sulfate, chloride and fluoride than the alternative colorimetric techniques and the precision and accuracy are greatly improved in the sub-mg/L range.

Because the chromatographic separation is controlled by particular characteristics of the species in question, it has not yet been possible to obtain a single scan for the determination of all the cationic species of interest (NH_4^+ , Na^+ , K^+ , Ca^{+2} , Mg^{+2}). A breakthrough with a different type of ion exchange column and a different eluant is likely, but for the present, two separate scans are needed. One determines ammonia, sodium and potassium and the other analyses for calcium and magnesium.

(F. Tomassini - (416) 248-3512)

STACK SAMPLING FOR ARSENIC

Recent findings at Yellowknife (N.W. T.), prompted the Federal government to request that Ontario document the stack emissions of arsenic from all gold mines in the province, which necessitated an extensive sampling and analysis program.

Samples of the stack gases and particulates are isokinetically sampled through a breech located approximately halfway up the stack. The probe is traversed stepwise across the interior of the stack and the samples are trapped in an impinger device. Impinger solutions and washings are analyzed and related to the total stack emissions.

Prior stack tests had utilized water-filled impingers and mechanical scrubbing of the probe with a brush and acetone to remove trapped particulate. Laboratory personnel suspected that this procedure, although satisfactory for determinations of total particulate and certain elements, might be inadequate for arsenic capture. In consultation with Air Resources Branch personnel, the following system was proposed.

The sampling train consists of six impingers, of which the first two contained concentrated hydrogen peroxide, the next two contain 1 N sodium hydroxide, and the fifth an empty trap to protect the silica gel in the sixth impinger. Arsenous oxide, As_4O_6 , the predominant form of arsenic in stack emissions, is more readily soluble in alkali than in water or acid. Thus

impingers three and four, which contain sodium hydroxide, trap the emitted arsenic. The peroxide is required to oxidize sulphur dioxide, a major component of stack gases, to sulphate. The resultant relatively involatile sulphuric acid is thereby retained in the peroxide impingers. If this precaution is not taken SO_2 will hydrolyze to sulphurous acid, H_2SO_3 , in the sodium hydroxide, neutralizing and thereby obviating its purpose.

The silica gel adsorbs water, protecting the pump and metering equipment and allowing the determination of the water content of the stack gases. After the completion of a sampling run, the probe and connections are washed with 0.1 N NaOH. About two minutes contact time must be allowed during washing to ensure complete dissolution of adsorbed arsenic compounds.

The first application of this system was at the Dickinson Mines in Balmertown, Ontario. The analytical results showed about 90% of the entrained arsenic to be in the first (strongly acidic peroxide) impinger. Apparently the solubility in acid and the 100°C temperature differential between the stack gas and the impinger solution was sufficient to condense and retain molecular and particulate arsenic compounds. The added trapping potential of the caustic trap apparently offered no additional benefits.

Subsequent laboratory experiments by the Federal Air Pollution Control Directorate confirmed that a simple water-filled impinger train was sufficient for the trapping of arsenic. Sodium hydroxide rinsing of the interior surfaces, however, was found to be essential for complete recovery of condensed arsenicals.

As a result of joint Federal Provincial consultation a simple, effective stack sampling procedure for the determination of arsenic emissions has now been developed. The impinger train now contains four impingers containing just water, followed by blank and silica gel traps. It is much simpler to work with and is as efficient as the earlier version, and experiments are now underway to reduce the number of water traps (which soon become acid due to SO_2) to three.

(Dr. B. Loescher - (416) 248-3346)

IDENTIFICATION OF MALODOROUS ORGANIC SUBSTANCES GENERATED IN THE SOUTH PEEL WATER POLLUTION CONTROL PLANT BY THE "ZIMPRO" PROCESS

Wet air oxidation processes to treat sewage sludge are gaining increasing popularity throughout North America. The sewage sludge treatment facilities at the Lakeview Water Pollution Control Plant just west of Metro Toronto consist of a "Zimpro" wet air oxidation process and a vacuum filtration dewatering works. The sludge when treated produces a filter cake that is sterile and disposed of on land.

Because of the increased ease of handling of the sludge over conventional treatment plants, this process can increase the capacity of an existing plant by modifying the sludge handling facilities. Also, the final effluent does not have to be sterilized by chlorination.

The major disadvantage of the "Zimpro" wet oxidation is that intense malodorous compounds are produced during the process. The exhausted air from the plant creates severe odour problems in the vicinity of the utility. The organic laboratory undertook to identify the organic components in the exhaust gas from the "Zimpro" process, with special emphasis on those compounds that are malodorous.

The organics were collected on a charcoal adsorbent, then extracted with ether, concentrated, and chromatographed on a silica gel column. The corresponding fractions were concentrated, then analyzed by gas chromatography/mass spectrometry.

The major components in the exhaust gases were aromatic and aliphatic hydrocarbons, ranging in molecular composition from C_6 to C_{29} . These compounds are generally not malodorous.

The major malodorous compounds identified were C_5 - C_9 saturated and unsaturated aldehydes, with hexanal being the major component. Also present were ketones, alcohols and esters, generally in the C_8 - C_{13} range. Volatile fatty acids from C_2 - C_{10} , and some phenols also contributed to the obnoxious odour.

The characteristic malodor could be reasonably reproduced by blending refer-

ence samples of aliphatic aldehydes identified in the "Zimpro" exhaust gases.

Skatole and indole were not found in the effluent, although some quinolines were identified. A lachrymator, bromoethyl benzene, was found. Relatively few sulphur containing compounds were identified.

The Lakeview WPCP is now committed to fume incineration of the "Zimpro" exhaust gases, and ultimately the dewatered sludge. The exhaust gases when incinerated (at 850°C) should eliminate the utility's malodor problems.

(Dr. O. Meresz - (416) 248-3031)

DETERMINATION OF PERFORMANCE CHARACTERISTICS FOR FECAL COLIFORM ENUMERATION PROCEDURES

An evaluation of four methods for enumeration of fecal coliforms has been carried out in six regional and central MOE microbiology laboratories, using the procedures recommended by ASTM for determining performance characteristics. Accuracy, specificity, counting range and comparability were determined in each laboratory for M-FC, mTEC (a procedure originally developed for thermotolerant *Escherichia coli*) and M-FC2 (the latter two methods include a 2 hour, 35°C resuscitation period). Results for these media were compared to the performance characteristics of MacConkey Membrane Broth (MMB), the medium presently in use for fecal coliform determinations.

Accuracy, for the purposes of this study, is defined as the difference between the mean of a population of estimates and the "true" population as measured on a non-selective culture medium. The accuracy of M-FC, mTEC and M-FC2 ranged from 85 to 95 percent compared to less than 60 percent for MMB. When the cultures were subjected to stress by exposure to cold temperatures for two days, the accuracy of each medium dropped by approximately 40 percent.

Over 1000 positive and negative colonies were identified in order to determine specificity. Specificity describes ability to optimally respond to the target organism

while minimizing detection of organisms giving a false positive reaction. The percentage true positive was highest on MMB at 89 percent; however, this medium also had the highest rate of false negatives at 26 percent. Overall specificity for the other three media ranged from 82 to 86 percent.

In preliminary counting range experiments using natural samples, M-FC2, M-FC and mTEC had median upper limits of 100, 75 and 70 respectively, compared to 80 for MMB.

Determination of comparability was based on 125 recovery comparisons using samples from a variety of sources. Recovery was significantly higher on mTEC and M-FC2; however, the latter also showed significantly higher background (negative) counts.

Additional counting range experiments are currently in progress and mTEC has been judged to give the best overall performance with highest recovery, low background, and very good specificity and accuracy. Use of mTEC as the standard fecal coliform medium will be implemented in the spring of 1979 to allow ample time for technician training and phasing-in of the new medium.

(J.E. Pagel - (416) 248-3008)

PRESERVATION OF FREE METALS IN NATURAL WATERS

In recent years increased importance has been placed on determining the role of heavy metals in the environment. Many metals have been shown to be toxic to a variety of life forms but the degree of toxicity depends on the physical form (dissolved, colloidal or particulate) as well as the chemical speciation (oxidation state, free or complexed) of the metals.

In order to determine dissolved free metals analysts faced two problems; first, the selection of an appropriate membrane filter for separating the dissolved metals (defined as those which pass through a 0.45 µm pore size filter) without contamination or other changes in chemical speciation, and second, the determination of the per-

ishability of the free metals (aquo-complexed) in stored filtered samples, which could with time be converted to complexed forms or could be adsorbed by the container walls.

The preservation study was restricted to lake waters taken in the area around Sudbury where measurable levels of dissolved free zinc and copper are present. Metal concentrations were measured by differential pulse anodic stripping voltammetry (DPASV), a technique which differentiates aquo-complexed metals from metals complexed otherwise. For analysis of the free metals, the samples were buffered at a pH of 6.0 using 0.03M sodium acetate.

The natural water samples were preserved until analysis by either i) refrigeration at 5°C, ii) freezing at -10°C, or iii) storage at room temperature (approximately 25°C). They were filtered prior to analysis through Gelman, Millipore, Sartorius or Nucleopore membrane filters. Losses of about 50% were observed for dissolved free zinc, copper, cadmium and lead at the 50 µg/L level for the first two filter types. The latter two gave quantitative recoveries. It was demonstrated that the observed losses were the result of complexation of the free metal ions by ligands leached from the membrane filter which rendered the metals undetectable by DPASV. The study also showed insignificant loss of "free" metals for up to 72 hours when stored at 5°C.

Arising from this work, the following procedure is specified when sampling natural waters (pH 4 to 7.5) for "free" metals analysis.

1. Filter samples in the field through Sartorius - cellulose nitrate membrane or Nucleopore - polycarbonate membrane filters.
2. Ship samples in nitric acid washed polyethylene bottles, refrigerated to 5°C, to the laboratory.
3. Analyse samples within 72 hours of sampling.

(R. Sadana - (416) 248-3346)

"ODOUR KITS" TO AID THE CHARACTERIZATION OF INDUSTRIAL ODOUR EMISSIONS

Odour problems represent an important area of interaction between Ministry of the Environment Staff and the general public.' In the West Central Region of Ontario alone, during a five month period (April to August) in 1977, 577 environmental odour complaints were received, representing over fifty percent of the total complaints.

The initial major problem is that complainants' odour descriptions are subjective, and MOE officers find it very difficult to suggest a possible origin of odour emissions so described.

To overcome this problem, Laboratory staff have designed an "odour kit" consisting of a selection of odorants mixed with hydrated magnesium sulphate and stored in 20 ml screw cap vials. Components were diluted with odourless, perfumery grade diethyl phthalate according to their odour intensity. Unsaturated compounds were stabilized by the addition of butylated hydroxyanisole (BHA) anti-oxidant.

Original selection of characteristic odours was made on the basis of industrial usage of various organic substances with high odour potentials. Attempts were made to include the most representative members in each group. While the difficulty in covering the wide array of industrial odours with a few samples was recognized, the original kit was designed to test the feasibility and usefulness of this approach. Field trials now underway will determine the optimal size and composition of the final system. The latter is expected to vary considerably with specific areas and Regions.

The trial kit contained odorants classified in three major groups as listed below.

Group A - Solvents

Toluene
Xylenes
Aromatic naphtha
Methyl ethyl ketone
Methyl isobutyl ketone
n-Pentanol
2-Ethylhexanol
Amyl acetate

Group B - Raw materials,
Intermediates

Styrene
Coal tar
Naphthalene
Cyclo-octadiene

Group C - Bulk Products
and Others

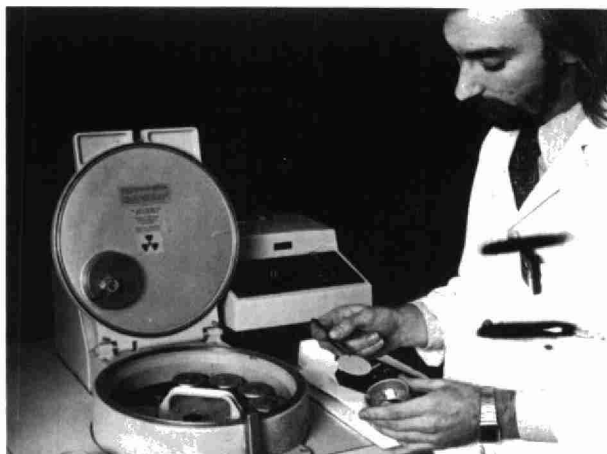
Gasoline
Stove oil
Valeric acid
Chlorophenol

(Dr. O Meresz - (416) 248-3031)

AUTOMATION OF THE X-RAY FLUORESCENCE SPECTROMETER

In general, multi-element analysis of samples of environmental interest by wavelength dispersive X-ray fluorescence spectrometry requires that optimal instrument settings be used for each element. The recent addition of a logic controller and a 10-position sample changer to the X-ray spectrometer in the Physical Methods Section now permits automatic adjustment of these parameters.

Coded instructions consisting of 18 characters are translated by the logic controller into a series of motor operations which set (or select) the sample changer position, and the collimator, crystal, and detector angle appropriate to the desired element. Also included in the coded instruction are characters which cause the pulse height analyzer and the counting time to be electronically set to desired values.



X-Ray with Sample Changer

A number of options are available for implementing this device in the laboratory situation. In one, a punched tape would be prepared which would instruct the logic controller in the appropriate operations. When the count was complete, the resulting signal would be output via the teletype and optionally punched onto paper tape. A new instruction would be processed and the cycle repeated until all desired measurements had been made.

Such an approach would be suitable for the routine determination of a single element in each sample. Straightforward calculations of concentration from calibration equations could be performed directly from the printed intensity data, while more complex calculations involving matrix and line interference corrections would be more effectively carried out by reading the punched tape into a programmable calculator. However, in this configuration, no possibility exists for changing experimental conditions within the run, should there be a need to do so.

A more sophisticated approach, which we have begun to implement, is to have the logic controller interfaced directly to a programmable calculator. This allows a much more flexible operation since the calculator can construct the instruction code based on the operator's requirements and transmit this instruction to the logic controller. The X-ray intensity is returned directly to the calculator which can accept the result or initiate a remeasurement using modified conditions. During the time the logic controller is operating the spectrometer, the calculator is performing the required calculation and preparing for the next transmission.

Direct computer control of the spectrometer permits one to include built-in checks on the quality of the data. It also permits operation after working hours.

At present, programs for the measurement of lead on high volume air filters and sulphur in vegetation have been written. We plan to prepare software for the multi-element analysis of vegetation and eventually to have a completely generalized operating system for X-ray fluorescence spectrometry.

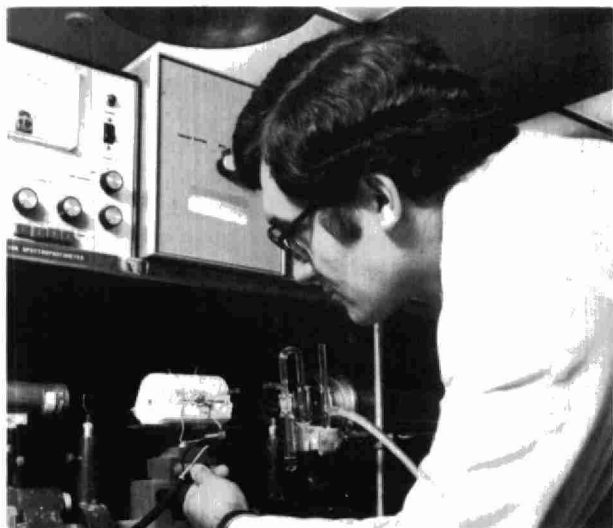
(Dr. P.J. Roberts - (416) 248-7101)

ANTIMONY IN ENVIRONMENTAL SAMPLES

The amount of antimony used in North America has increased over the last decade. It is used increasingly in the production of metalware, paints and pigments, plastics, rubbers, glass, pharmaceuticals and fireworks, and in the flame proofing of fabrics.

Although metallic antimony is relatively inert, stibines (antimony hydrides) are highly toxic. Cases of dermatitis have been reported in the manufacture of antimony trioxide, and certain forms of antimony cause irreversible damage to the heart and tubular cell damage to the kidneys. In order to evaluate possible problems associated with the increased adventitious losses of antimony to the environment, more sensitive techniques are required for detecting its presence in air, water, vegetation and soil.

The Laboratory Services Branch has had success in applying the hydride generation atomic absorption technique to the determination of arsenic and selenium. The same approach has now been extended to the measurement of antimony.



*AAS Unit with Flameless Accessory
for Antimony Determination*

Samples of soil, sediment, vegetation water and airborne dust are digested with a mixture of sulphuric, nitric and/or perchloric acid in calibrated test tubes.¹ The digestates are diluted to 15 mL with distilled water and processed in an automated analytical system where antimony is converted to a gaseous hydride and passed through a heated quartz tube atomizer at a

rate of 20 samples per hour. The atomic absorption is recorded at 217.6 nM.

The method is free from interferences from commonly occurring elements although tellurium may interfere when present at concentrations greater than 1 mg/L. The relative standard deviation of the method is 8.5% at levels between 0.15 and 5.0 mg Sb/L. Accuracy was established by replicate analysis of NBS Orchard Leaves and Pine Needles and by parallel analysis of different sample types using the Rhodamine B method.¹ The mean recovery of added antimony in lake and rain water samples was 97.4%. The sensitivity and detection limit are similar to those for arsenic and selenium by the same technique. Using this technique, the ambient air concentration of antimony for twenty different Ontario locations has been found to vary between 0.04 and 730 ng/M³. The sites included residential, commercial and industrial locations in towns and cities.

(P.N. Vijan - (416) 248-3775)

CHLORINE DETERMINATION IN WATER SAMPLES

Although chlorination is a widely practiced, effective technique for disinfection of sewage in North America, the toxicity of chlorine to fish, and the possibility of formation and bioaccumulation of organics, have given rise to some concern. Consequently the feasibility and effectiveness of alternative techniques, as well as the necessity for disinfection under certain conditions, is under investigation throughout North America.

Since the review of chlorination and other alternative disinfection procedures will take considerable time, in the interim better control of chlorination and, where possible, reduction in its use, is important from both environmental and economic points of view. Therefore, the techniques used to monitor chlorine residuals must be improved. The orthotolidine (OT) technique, currently in use in most Ontario's treatment plants, is being discontinued throughout the world not only because of its unsatisfactory performance but also because of the potential carcinogenic effects of the reagent itself.

The Laboratory Services Branch has investigated the alternative test methods available, including a modified amperometric and the Palin's Comparator techniques. Findings to date confirm that orthotolidine is the least rugged technique of all the methods examined. Intercomparison shows that the modified amperometric and DPD Comparator agree closely throughout the working range of the test and generally that the OT is incorrect. Several serious problems associated with the orthotolidine method have been outlined by G.C. White in the Handbook of Chlorination published by Van Nostrand Reinhold Ltd. (1972). White notes "that residuals being chloramine residuals and probably organic chloramines at that, the color forming reaction with OT is very slow. In many cases full OT color is never reached under ordinary conditions. Secondly, the lowering of the pH (during analysis) makes the chloramines more reactive so that a large fraction of chlorine residual may react with sewage constituents rather than with the OT. Unless indicator concentration and acidity are properly controlled, oxidation products are formed, resulting in unstable colors and lack of reproducibility".

We recommend that in institutions where the cost could be justified and trained individuals are available, the amperometric titrator should be installed as a first choice and when costs are restrictive, the use of the DPD Comparator should be implemented. Regardless of which method is adopted, an on-site comparison should be undertaken to ensure ruggedness under actual field conditions.

Our in situ observation of the OT technique suggests that, since the OT method tends to read low, excess chlorine will be applied in practice. With the acceptance of either the amperometric or the DPD Comparator method as the standard analytical technique in sewage treatment plants, two things would be accomplished, namely a more exacting measurement of residual chlorine and a reduction in chlorine usage.

(S. Villard - (416) 248-3512)

ELUTRIATION FOR FINES FRACTIONATION

The process of elutriation involves washing of a mixture to separate some or all of its constituent components. This procedure has been used for centuries by prospectors in panning for gold. It was also one of the earliest methods used to separate clay from silt and sand and is again coming back into use. Simply, an upward current of water will carry away the smaller particles whereas the larger particles will settle at a rate determined by the difference between gravity fall defined by Stokes law and the constant upward velocity of water maintained by the conditions of the test.

Elutriation has been used recently in the physical fractionation of soils and sediments in the study of plutonium geochemistry by the Argonne National Laboratory. Our laboratory employed a similar procedure to isolate various size fractions on samples taken at Elliott Lake to determine the distribution of radium with particle size.



Elutriation Process

Several workers have shown that analysis of the fines fraction for toxic metals can help differentiate between pollutant input and background geochemical levels. Data can be interpreted on a common basis since the variable coarse fraction is eliminated. The fines content is important in environmental studies in that it is most subject to transport by erosion; in addition,

the fines tend to contain higher concentrations of metals than those of the soil or sediment as a whole. This concentration effect is useful in itself in determining concentrations of environmentally significant trace metals such as cadmium at background levels for which the current routine analytical method has inadequate sensitivity.

Elutriation is a cheap, simple (but slow) procedure to obtain the quantity of fines needed for chemical analysis. The Laboratory was requested to determine metal concentrations in <20 µM fines in

sediments in the South-western Region to assist in monitoring long term water quality trends. The procedure is also proving useful in determining changes in cadmium/zinc ratios in sewage sludge disposal fields (important in relation to cadmium uptake by plants). Without the concentration effect of fractionation, cadmium is usually below the detection limit and it is not possible to determine the ratio.

Some examples of concentration effect are as follows:

SEDIMENTS (SW REGION)			7 sites
Ranges in concentration µg/g			
	Entire sample <1 mM	<20 µM	Magnification Factor
Cadmium	<0.4	0.9 - 4.6	-
Chromium	4.5 - 33	23 - 420	1.4 - 15
Copper	3 - 25	20 - 360	1.7 - 33
Lead	3 - 56	12 - 190	1.7 - 53
Zinc	20 - 110	89 - 620	1.5 - 23
Mercury	<.01	.09 - .78	-
SLUDGE DISPOSAL FIELDS - CHATHAM			4 sites
Cadmium	<0.4	0.8 - 1.4	-
Chromium	8.5 - 19	45 - 87	4.1 - 5.8
Copper	6 - 11	32 - 59	5.2 - 8.0
Zinc	23 - 31	140 - 160	5.2 - 7.0

(Frank Darcel - (416) 248-3346)

PERFORMANCE OF THE AUTOCLAVE DIGESTION METHOD FOR TOTAL PHOSPHORUS ANALYSIS

In an effort to improve the analytical precision of the Total Phosphorus test as applied to low concentrations characteristic of oligotrophic Northern Ontario lakes, an autoclave digestion procedure has been developed which minimizes sample handling during the conversion of organically bound phosphorus to the orthophosphate form. Phosphorus recovery studies between the autoclave procedure and the manual hot-plate digestion procedure showed that the autoclave technique is

suitable for most samples except those containing high levels of suspended solids such as raw sewage and flood stage rivers. Although both methods utilize sulfuric acid-persulfate digestion reagents, the autoclave procedure is a less severe digestion technique in that it is carried out at constant volume, whereas in the manual procedure the sample is taken to the fuming acid point before adding the persulfate.

The autoclave procedure has been found to be highly successful for the determination of particulate phosphorus levels. This is achieved by performing both a Total and a Filtered Total Phosphorus

analysis on separate portions of the sample. In this procedure, the filtrate from field filtered (0.45 μ Sartorius Cellulose Acetate filters) samples is analyzed by the same autoclave phosphorus procedure as used for the whole sample. Field filtration is essential in order to maintain the phosphorus fractionation existing at the time of sampling. Test precision of 0.001 mg P/L for low-level field filtered samples have been achieved. Laboratory-prepared precalibrated 25 x 150 mm pyrex screw top culture tubes fitted with a teflon lined cap are used for both sample collection and subsequent analysis. Since the culture tube serves as the field collection and shipping container digestion vessel and automated sampler tube, in-laboratory sample transfers are eliminated. Based on studies using sensitive analytical techniques for determining orthophosphate, a working range of 0.5 to 20 μ g P/L is feasible, although the procedure appears to be limited by background levels which can run as high as 1 μ g P/L.

(Dr. F. Dieken - (416) 248-3512)

A SIMPLIFIED DIGESTION PROCEDURE FOR THE ROUTINE ANALYSIS OF METALS IN WATER

The Effluent Laboratory routinely determines as many as thirty metals on a variety of sample types. Rigorous digestion methods are required on some samples, like sewages or industrial wastes, to remove organic matter and to solubilize metals adsorbed or absorbed onto particulate matter. However, they are not essential for relatively clean water samples.

For water samples containing low μ g/L levels of metals, a variety of preconcentration/preparation methods are available. Experience in the Laboratory Services Branch has indicated that a simple preconcentration using nitric acid as the sole digestion agent is superior to the more elegant approaches such as chelation/solvent extraction or coprecipitation.

This approach has the additional advantage of avoiding multiple digestions, which are required when applying rigorous digestions, in order to prevent precipitation or volatilization of elements of interest to the analyst. These multiple, rigorous digestions usually involve aqua regia or sulfuric-nitric acid combinations, and are more labor intensive. They tend to be subject to imprecision or error because of the number of steps involved in their completion and the amounts of glassware (beakers, watchglasses, test-tubes) required.

Success with the simple preconcentration procedure has led to the development of a simpler, more direct technique for handling large numbers of samples. An oven digestion procedure has been developed in which 50 sample aliquots are poured into test tubes calibrated for 25 and 50 mL. Five mL of nitric acid is added and the samples are placed in a clean, ventilated, oven set at 90°C. In approximately 36 hours, after it has been reduced to 2 or 3 mL, the sample volume is brought back to 25 mL with distilled deionized water and the sample is mixed and analyzed.

Analysis of control samples by both current and proposed digestion procedures shows good agreement for Zn, Fe, Cd and Pb. The technique requires about one-fifth the technician time of the regular procedure and for relatively clean samples it has proven to be more precise than the data obtained using the regular digestions.

The improvement in precision is primarily due to the decrease in number of steps involved. Nitric acid tends to be relatively free of metal contamination, so blanks also tend to be lower. For example, iron by the oven preparation has a blank of $.086 \pm .044$ mg/L while by the H_2SO_4 - HNO_3 preparation it was $.21 \pm .10$ mg/T. The oven digestion procedure is now on-line for all "clean" water samples and experiments using a combination of oven and hot block digestions are in progress in an attempt to simplify the preparation steps of samples with more complex matrices.

(Dr. B. Loescher - (416) 248-3346)

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